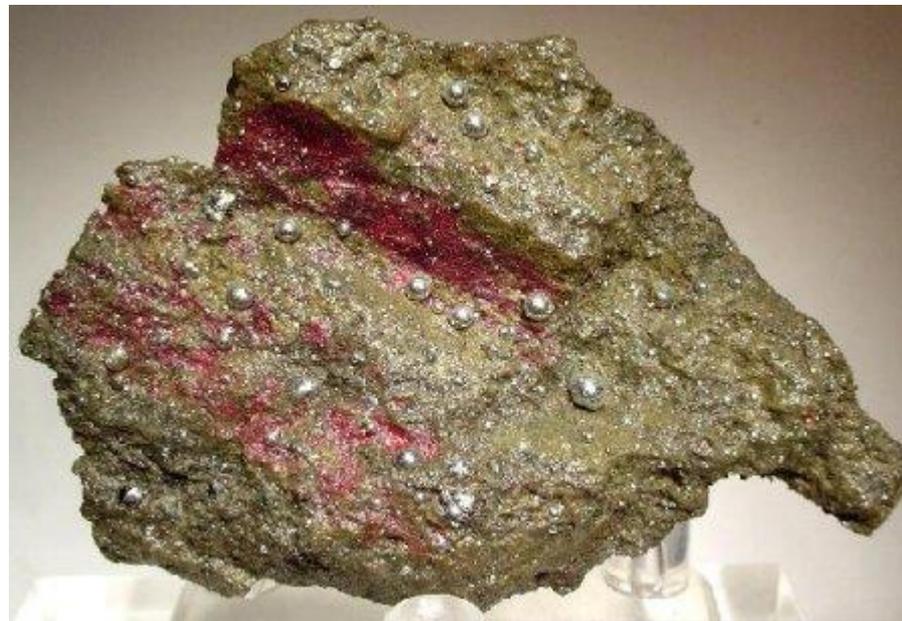


# Perché Hg?



Cinabro (HgS) e goccioline di mercurio nativo



# Cicli **naturali** del Hg

- **Emissione naturale:**

- Primaria

- Dai vulcani all'atmosfera
    - Da suoli/rocce con alti contenuti in mercurio – anomalie geochimiche

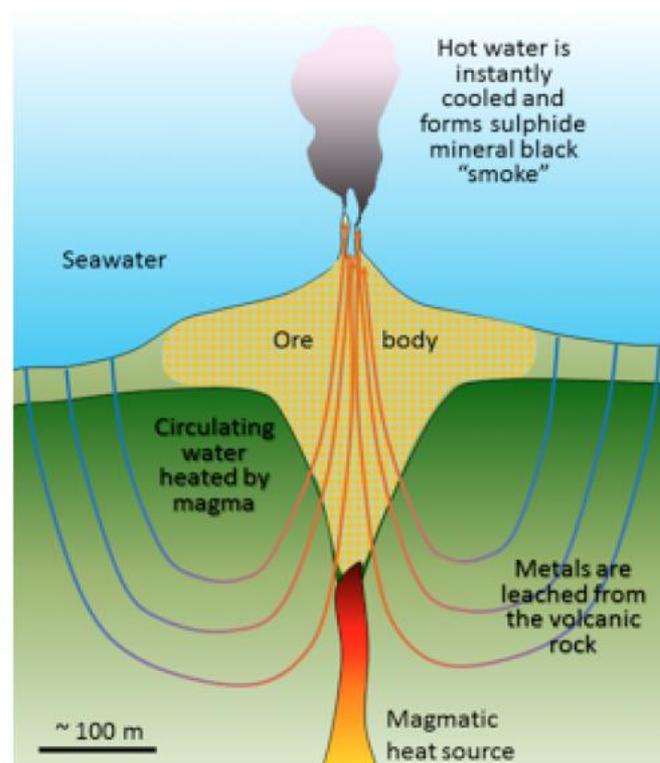
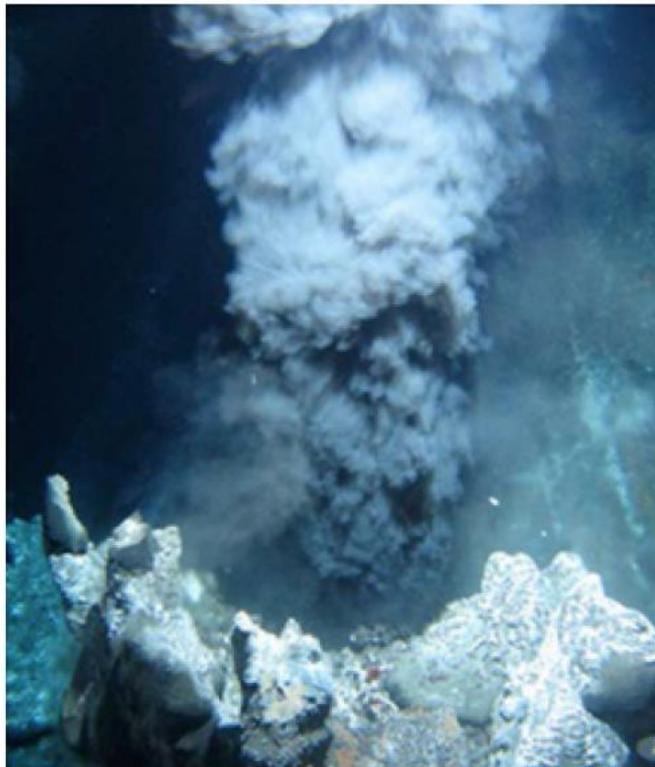
- Secondaria

- Dalla vegetazione che vive su suoli ad elevato contenuto di mercurio
    - Durante incendi forestali
    - Dagli oceani

# Cicli **naturali** del Hg

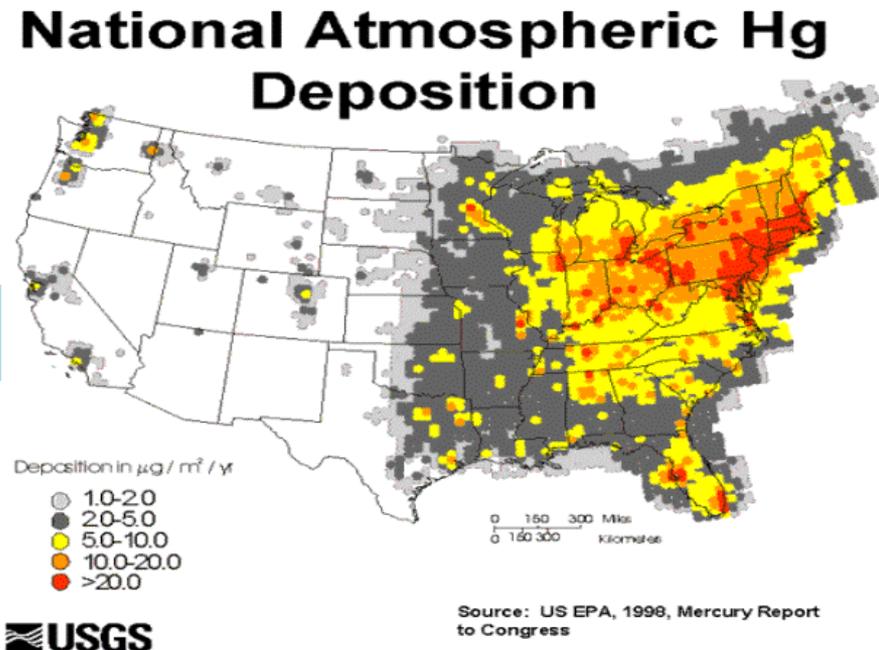
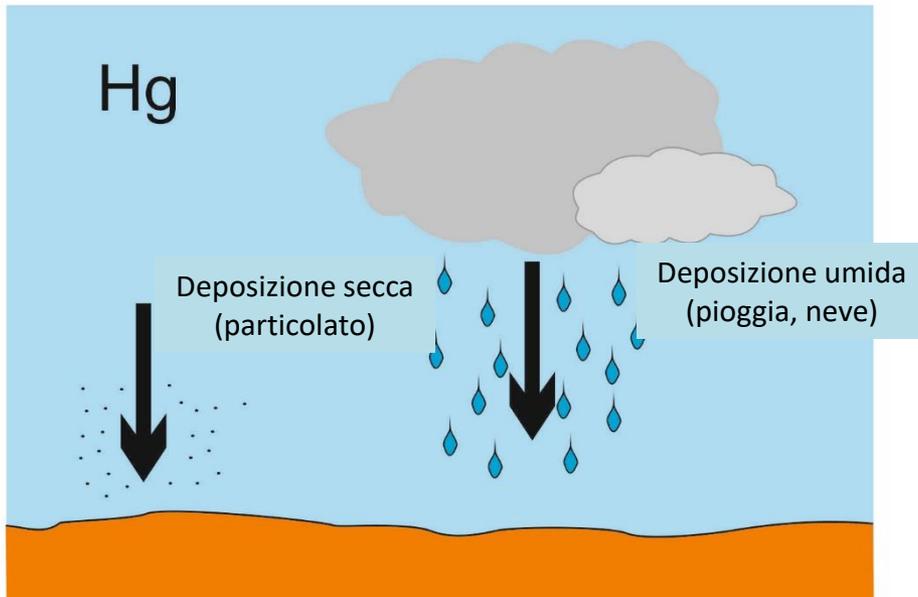
- **Deposito naturale – Giacimenti:**

- Combinazione del Hg con zolfo (S) per dare HgS
- Combinazione con S e Zn per dare sfalerite (ZnS)
- Negli oceani con soluzioni idrotermali (metacinnabro)

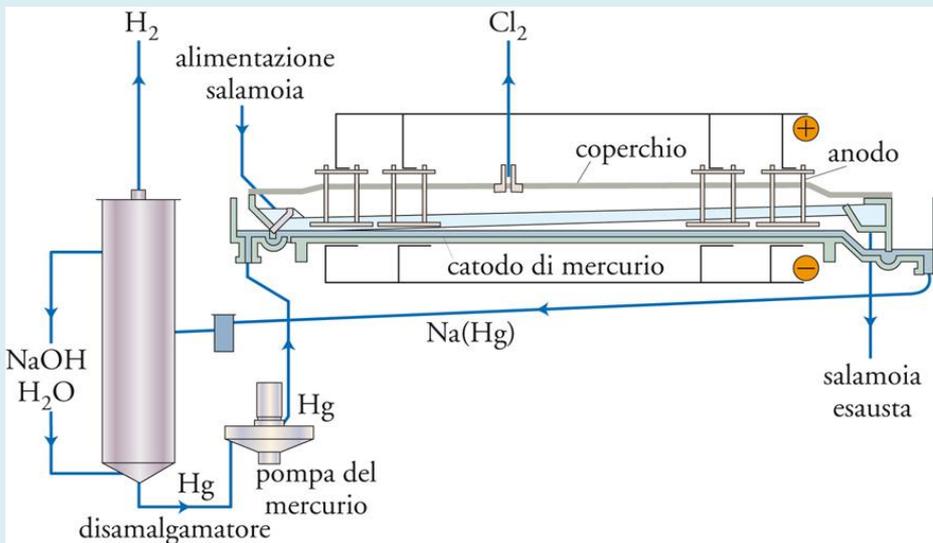
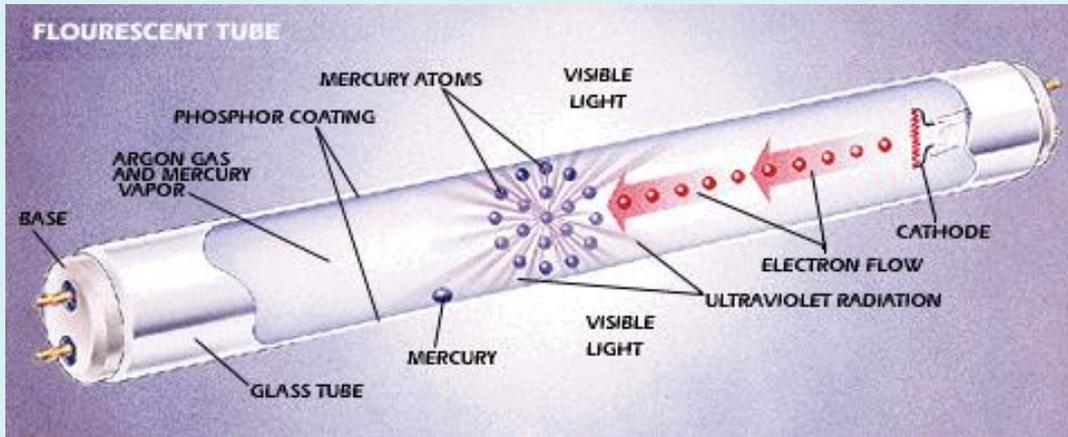


# Cicli **naturali** del Hg

- **Deposito naturale – “Deposizioni atmosferiche”:**
  - Secca: associata a particelle “sedimentabili”
  - Umida: con le precipitazioni

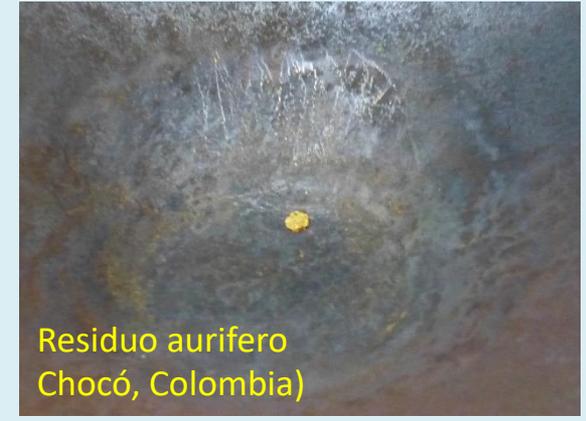
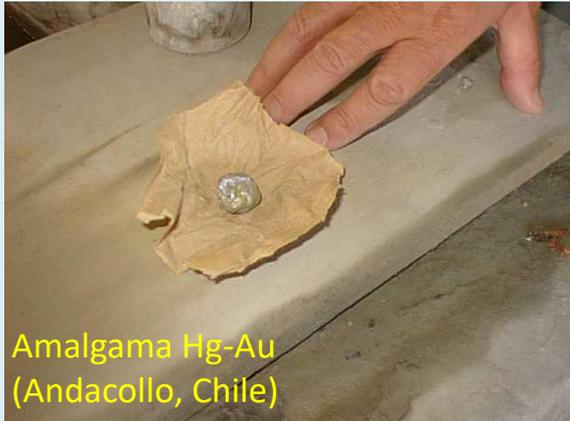


# Utilizzi industriali del Hg



# Utilizzi industriali del Hg

## Attività estrattiva artigianale dell'oro



Compravendita di oro, Río Súchez, frontiera Bolivia-Perú



# SORGENTI DI MERCURIO NELL' AMBIENTE

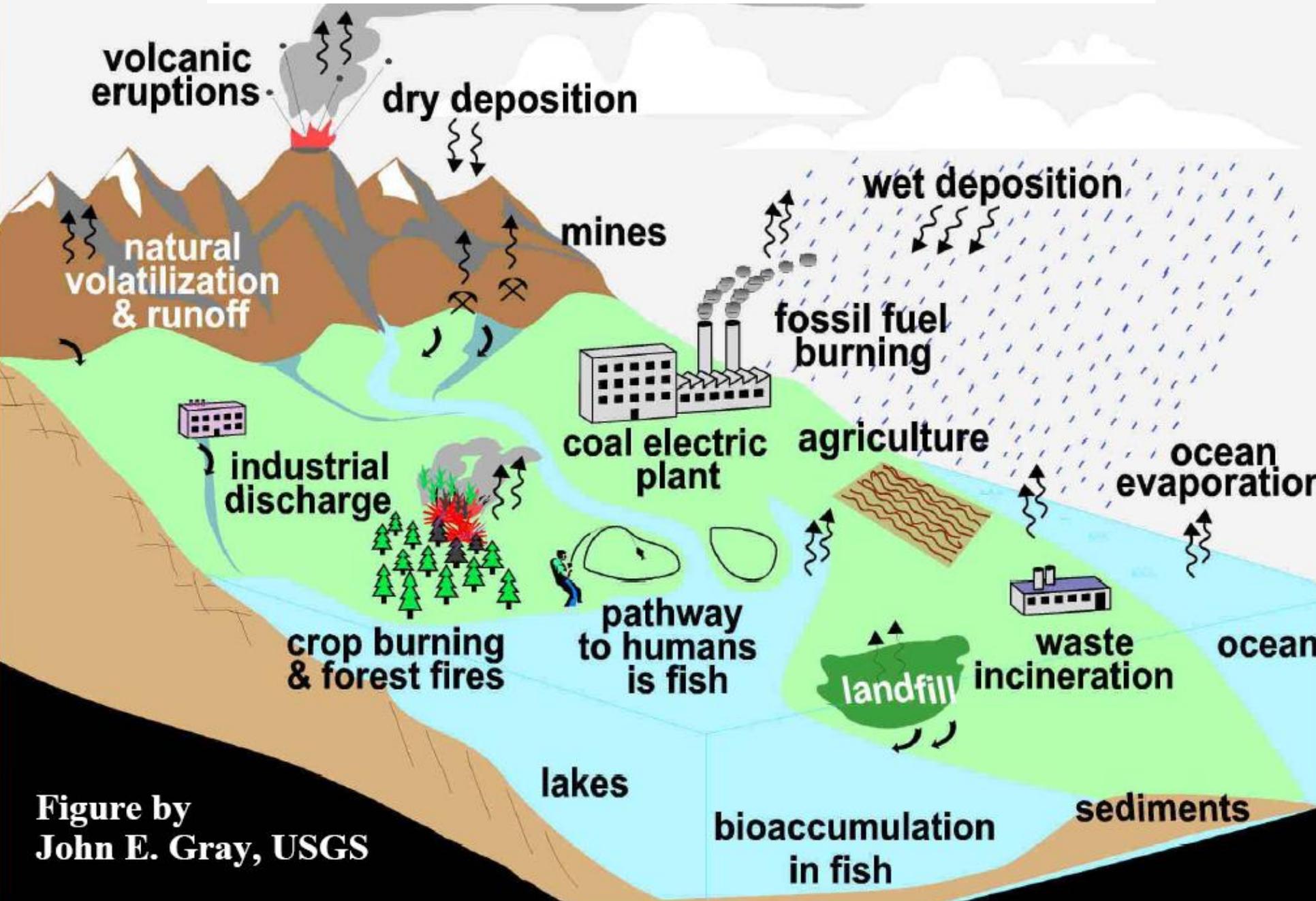


Figure by  
John E. Gray, USGS



Perchè il cappellaio matto?

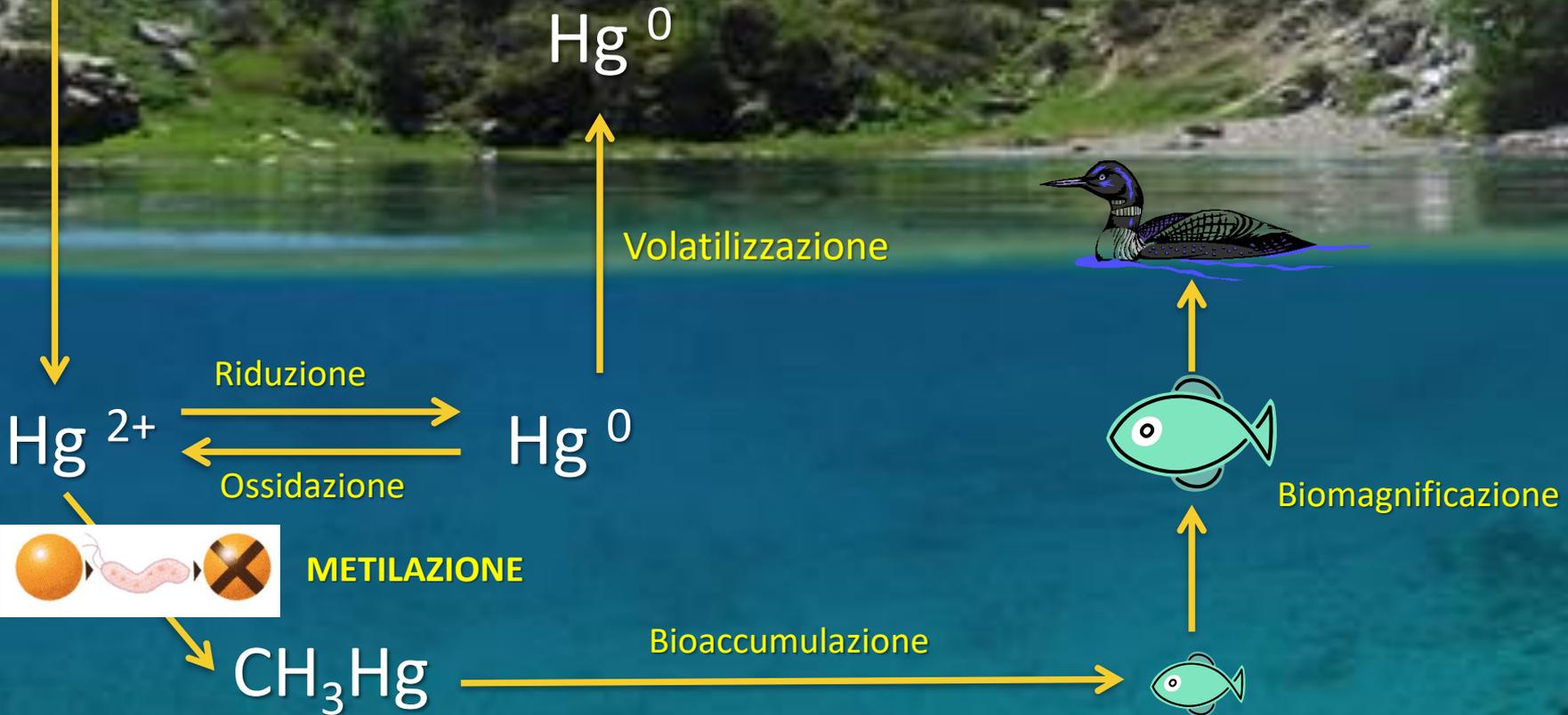
# Aspetti tossicologici del mercurio (Hg)

- Hg<sup>0</sup>**
- Mercurio elementare (termometri, amalgama, batterie,..)
  - Forma gassosa principale altamente insolubile (combustibili fossili, attività mineraria, ...)
  - **Trasporto ad ampia scala**
  - Perdurante esposizione ai vapori provoca una risposta neurotossica (“mercurialismo”): polmoni → sangue → cervello
- Hg<sup>2+</sup>**
- Mercurio ionico (sali disinfettanti, antibatterici, antiparassitari)
  - Fase liquida, solubile
  - Biodisponibile
  - Nuoce alla pelle e alla mucosa (reni e fegato)
- CH<sub>3</sub>Hg<sup>+</sup>**
- **Monometilmercurio**
  - **Si accumula nei tessuti biologici (assorbimento via intestino e placenta)**
  - Neurotossina – è la forma più tossica del Hg, responsabile di ritardo nello sviluppo psico-motorio nei bambini, di danni all’udito ed alla vista.

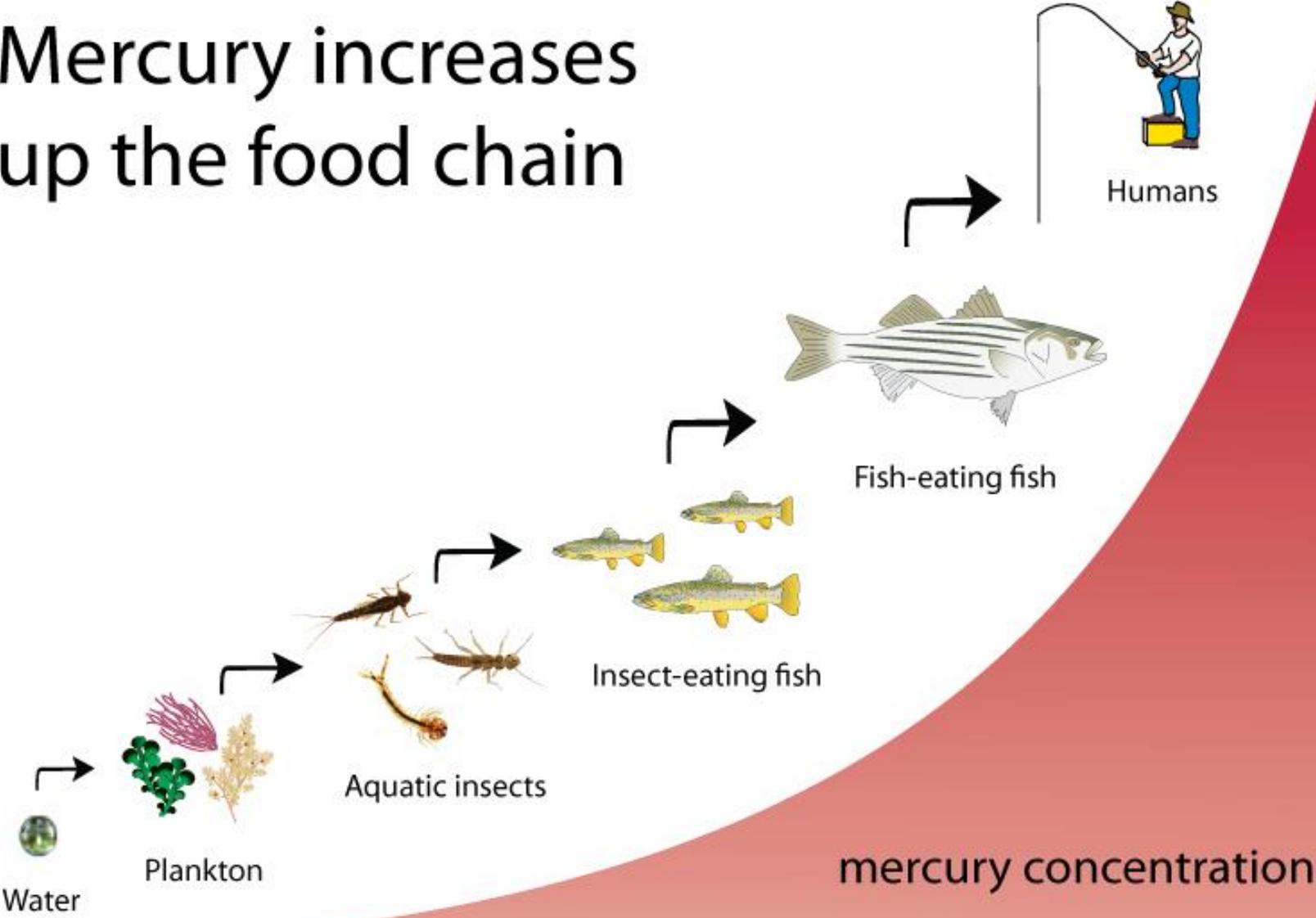
# Ciclo biogeochimico del Mercurio



Deposizione



# Mercury increases up the food chain

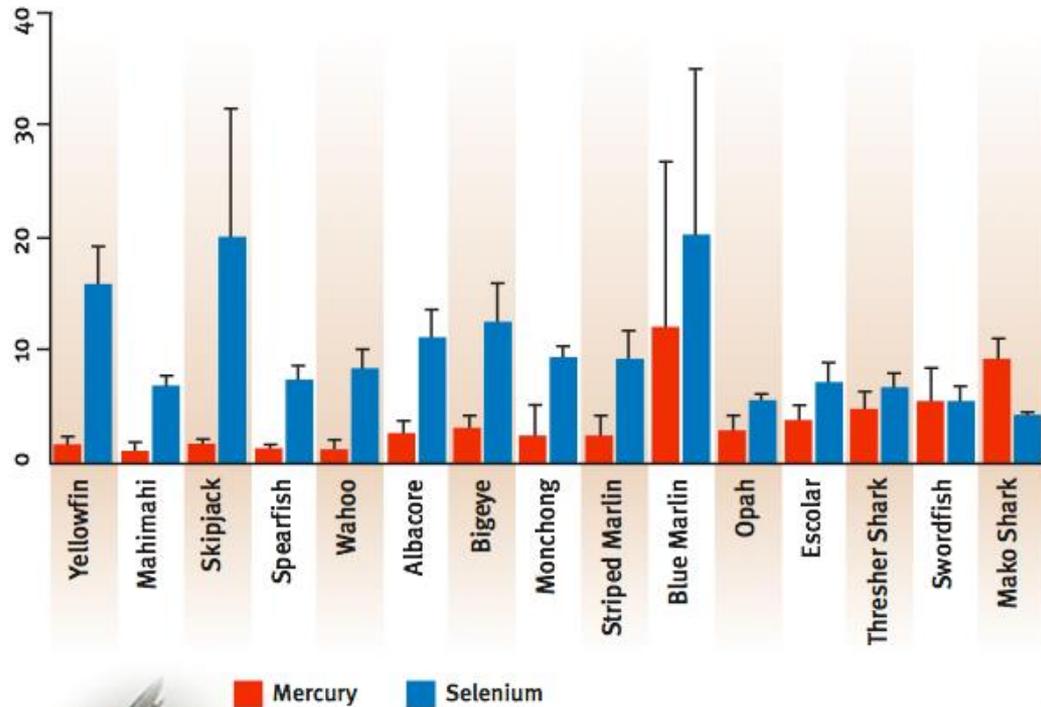


# Selenium in Ocean Fish Protects Against Mercury

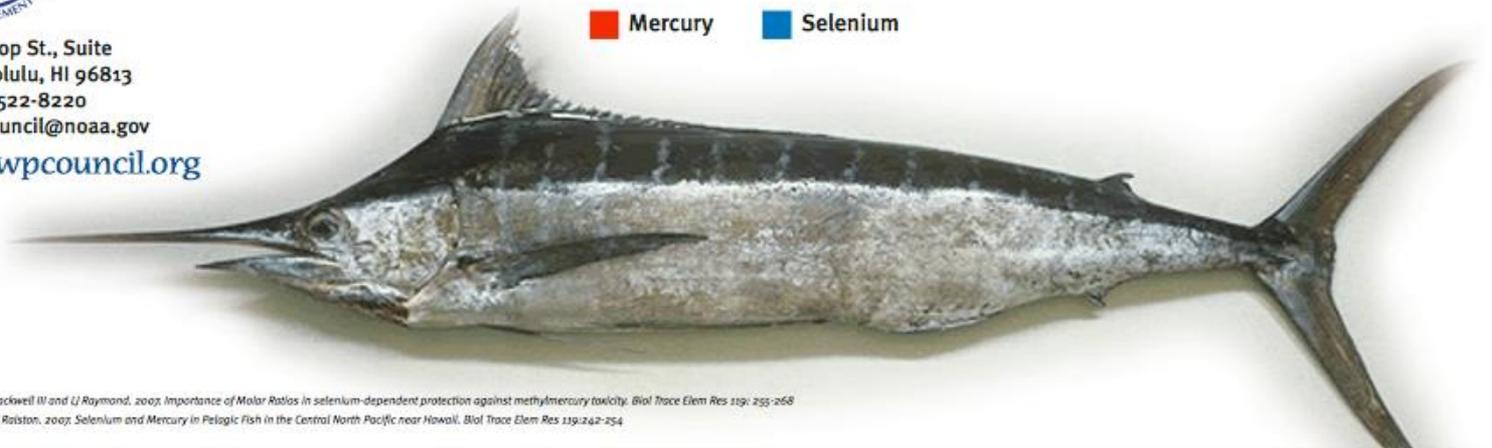
Selenium, an essential element in our diet, is vital to the body's antioxidant system and proper immune system function. It has anti-cancer effects and is known to detoxify metals including mercury.<sup>1</sup>

Regardless of the amount of mercury in fish, if the selenium level is higher, the fish is safe to eat. On the graph, molar concentrations of mercury and selenium in 15 Hawaii fish species are expressed as means  $\pm$  standard deviations. The graph lists the species from lowest to highest mercury-to-selenium ratios.<sup>2</sup>

All of our popular ocean fish are an excellent source of health promoting selenium as well as high quality protein and omega-3 fatty acids. (Mako shark is not popular or commonly eaten in Hawaii.) Our favorite fish are more likely to protect against mercury toxicity, than cause it.



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 info.wpcouncil@noaa.gov  
[www.wpcouncil.org](http://www.wpcouncil.org)



<sup>1</sup> Rolston NWC, JL Blackwell III and LJ Raymond, 2003. Importance of Molar Ratios in selenium-dependent protection against methylmercury toxicity. *Biol Trace Elem Res* 119: 255-268

<sup>2</sup> Kaneke J and NWC Rolston, 2007. Selenium and Mercury in Pelagic fish in the Central North Pacific near Hawaii. *Biol Trace Elem Res* 119:242-254

# Selenium Content of Common Foods

Micrograms per 100 grams food, uncooked

	Food	Selenium
	Brazil Nuts	1918.9
	Chicken liver	54.6
	Mackerel	44.1
	Shrimp	38.0
	Tuna, Yellowfin	26.5
	Halibut	36.5
	Eggs	31.7
	Mushrooms, brown	26.0
	Clams	24.3
	Turkey breast	22.4
	Chicken breast	17.8
	Ground beef	14.2
	Mushrooms, white	9.3
	Asparagus	2.3

Based on data retrieved from [Nutritiondata.com](http://Nutritiondata.com)



# 2001 Global Mercury Conference Minamata (JPN)

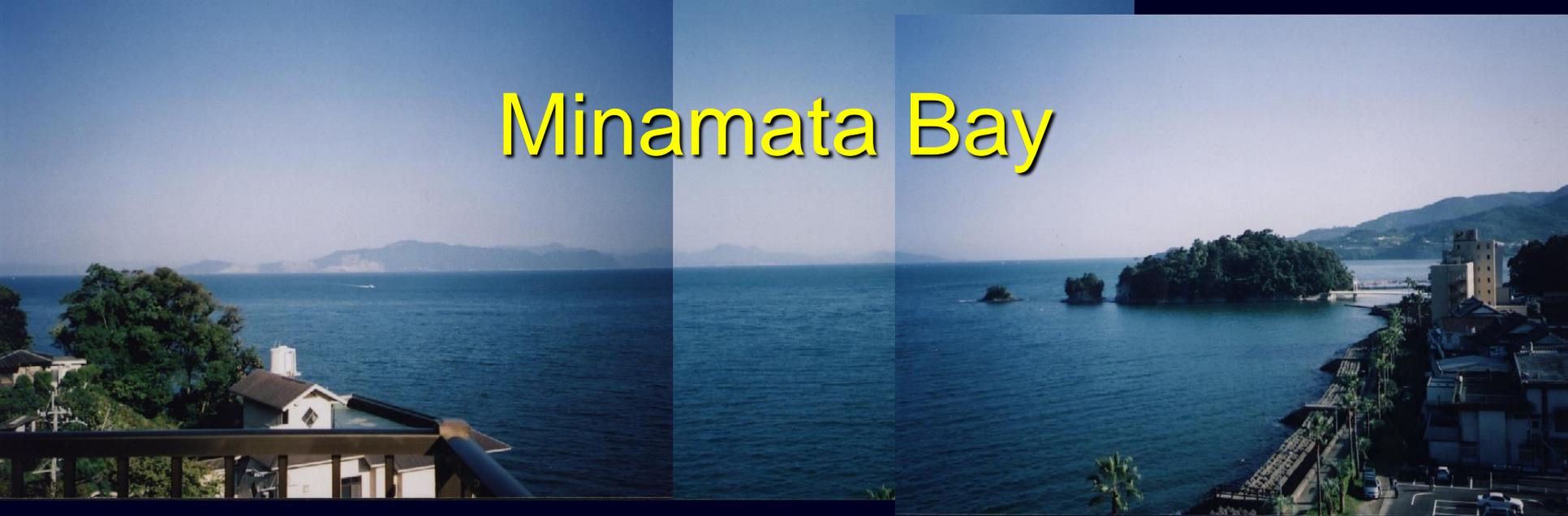
Nel 1932, Chisso iniziò a produrre acetaldeide utilizzata nella fabbricazione delle plastiche.

Il Mercurio era utilizzato come catalizzatore.

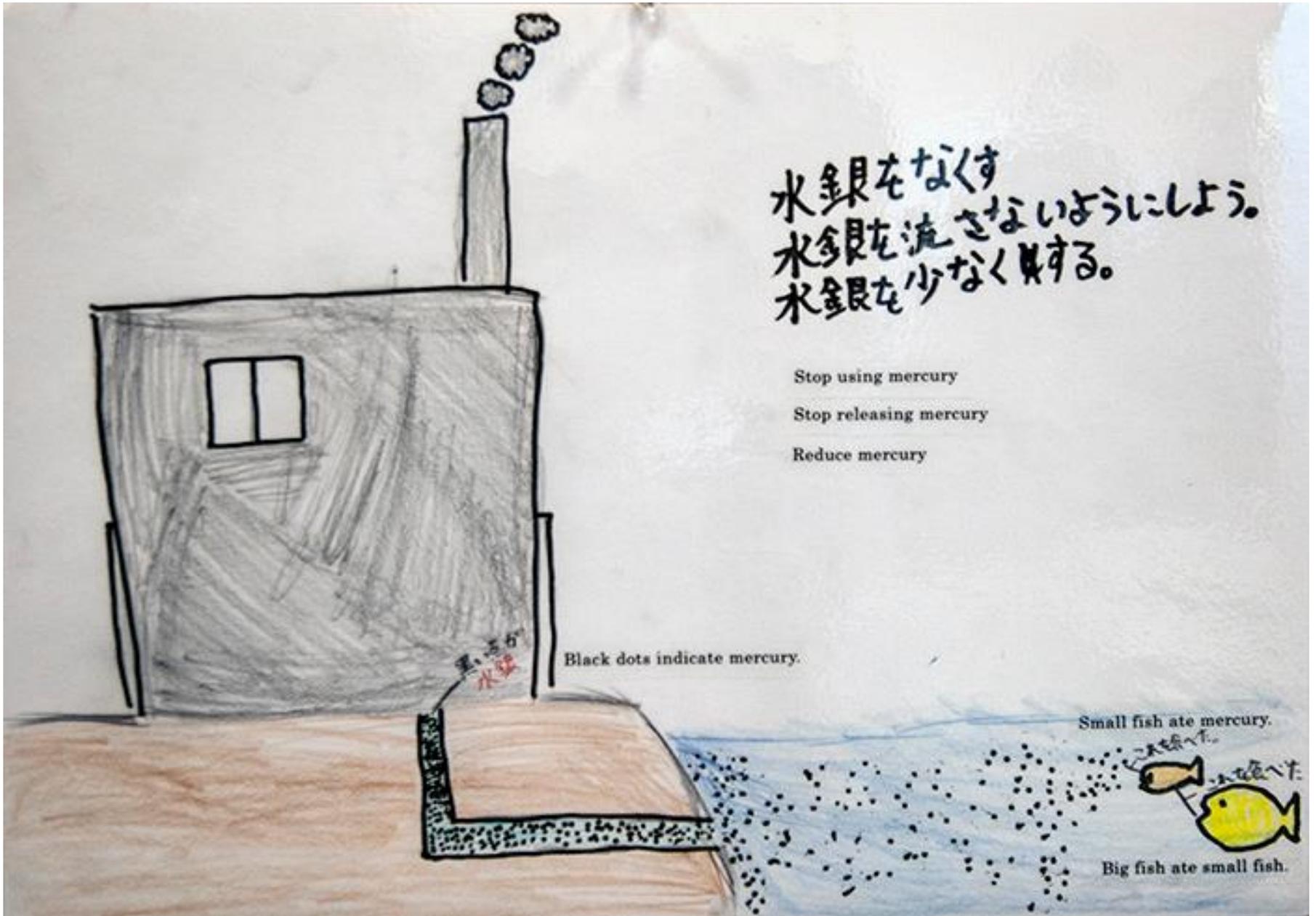


## Chisso Chemical Plant

# Minamata Bay



- I problemi di salute si osservarono a Minamata (1953) e, più tardi, a Niigata (1965) quando venne estesa la condotta dei reflui.
- La contaminazione si interruppe nel 1968.
- Sversate fino a 600 t di Hg e Metil-Hg.
- La popolazione locale consumava pesce e molluschi contaminati.
- Fino al 2001, 1784 i decessi, > 12.000 i casi di avvelenamento di Mercurio ufficialmente accertati.



# “Il morbo di Minamata”: sintomi

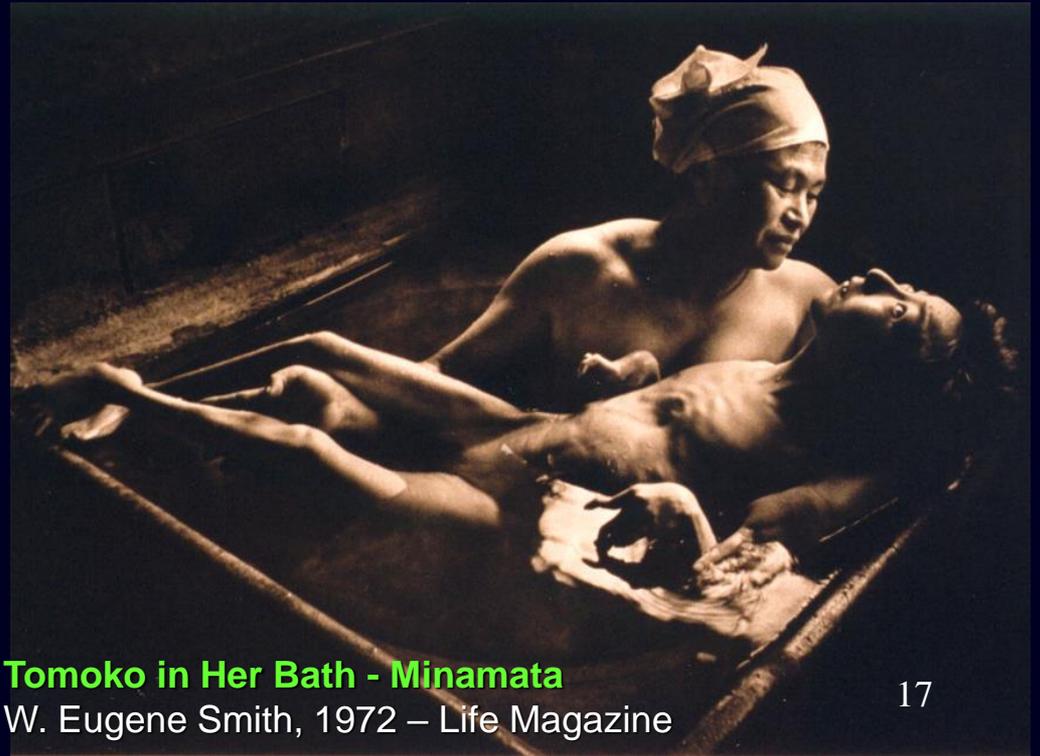


- Intorpidimento delle estremità
- Difficoltà nei movimenti degli arti (mancanza di coordinamento), debolezza e tremori
- Disturbi della parola, della vista e dell'udito a causa di danni al cervelletto
- Paralisi generale, difficoltà di deglutizione, convulsioni e morte

## ***Fetal Minamata Disease***

“paralisi cerebrale”

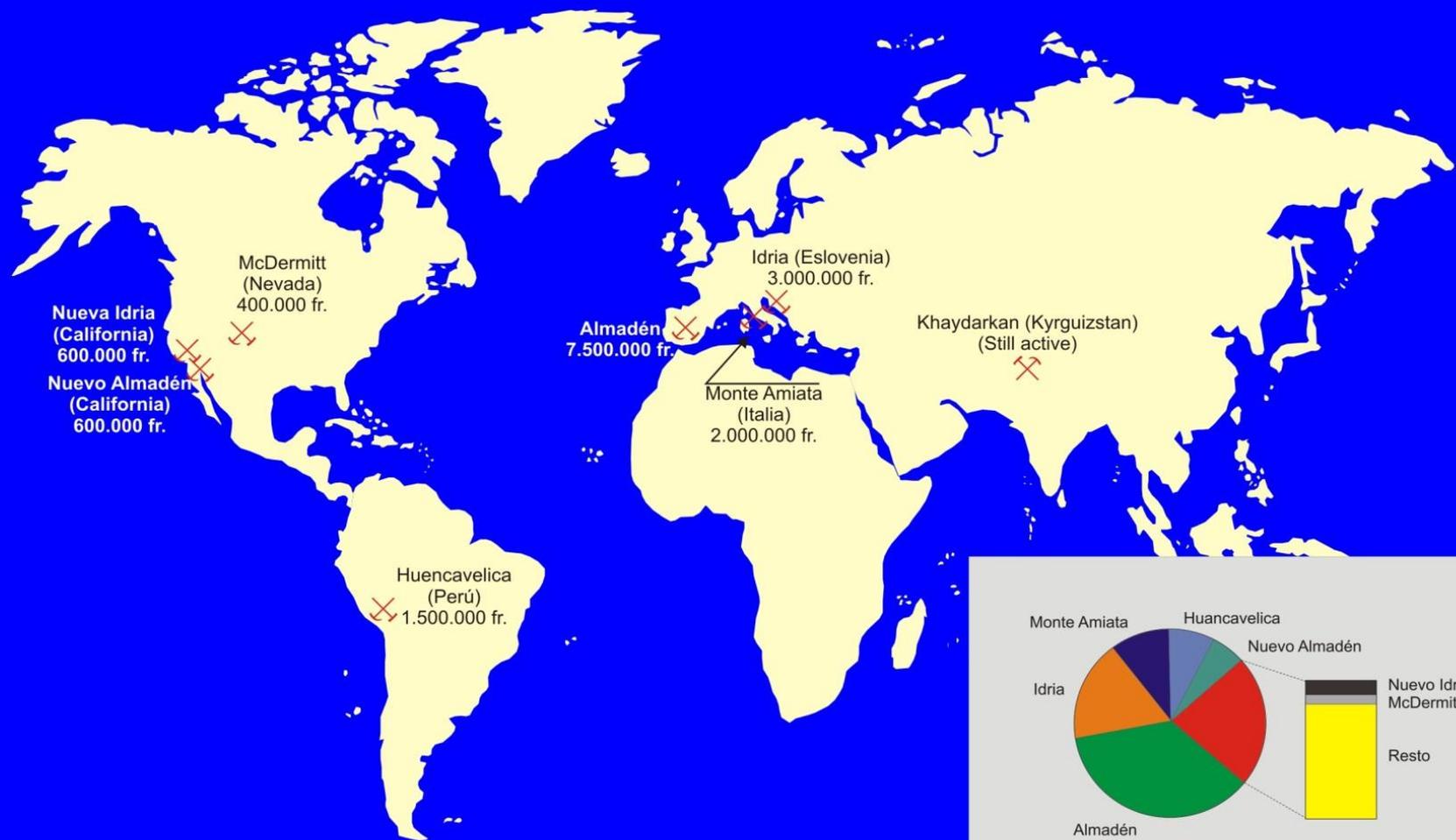
(6 % dei neonati a Minamata  
0.5% in Giappone)



**Tomoko in Her Bath - Minamata**

W. Eugene Smith, 1972 – Life Magazine

# Le aree minerarie del Hg



# L'area mineraria di Almaden

- Classica estrazione dal sottosuolo
- Miniera a cielo aperto (El Entredicho)



# L'area mineraria di Almaden

## Riconversione in Parco Minerario

The screenshot displays the website for the Almaden Mining Park. The browser's address bar shows the URL [www.parqueminerodealmaden.es/index.php?idioma=es](http://www.parqueminerodealmaden.es/index.php?idioma=es). The page features a navigation menu with links to 'Parque Minero', 'Hospital de Mineros de San Rafael', 'Ofertas/Promociones', 'Contacto/Reservas', and 'Cómo llegar'. A central section titled 'Presentación / Inicio' provides information about the park's history and its status as a UNESCO World Heritage site. To the right, a banner promotes a train ride through the mine, and a footer encourages visitors to provide feedback.

www.parqueminerodealmaden.es/index.php?idioma=es

Toshiba UCLM UCLM Scopus EL PAÍS Google Facebook Dropbox Otros marcadores

Parque Minero Hospital de Mineros de San Rafael Ofertas/Promociones Contacto/Reservas Cómo llegar

**Parque Minero de Almadén**

Presentación / Inicio

El **Parque Minero de Almadén** es la herencia viva de los dos mil años de la explotación de Almadén. Tras el cierre de la actividad minera en 2003, **las minas más antiguas del mundo** cuya actividad se ha mantenido hasta nuestros días, muestran sus secretos.

El mercurio, la plata viva de los romanos, se muestra en el Parque en todos sus aspectos, la extracción de su mineral, el cinabrio, sulfuro de mercurio, su transformación en los hornos metalúrgicos, sus propiedades físicas y químicas, sus usos y, como no, su eterna historia.

Las instalaciones del Parque Minero, los pozos, edificios e instalaciones son el corazón de los bienes españoles inscritos en la lista de **Patrimonio de la Humanidad** con el nombre de **Patrimonio del Mercurio, Almadén e Idria**.

Un impresionante viaje a las entrañas de la tierra...

Ayúdenos a mejorar cumplimentando un breve cuestionario y escribiendo su opinión

Opinión Cuestionario

183px-UNEP\_logo.svg.png

Mostrar todas las descargas...

# L'area mineraria di Almaden

Declaration of Almadén mines as World Heritage (UNESCO, 2012)



Heritage of Mercury



Almadén Idrija



## Nord Adriatico:

due le sorgenti identificate di Hg

1) storica:

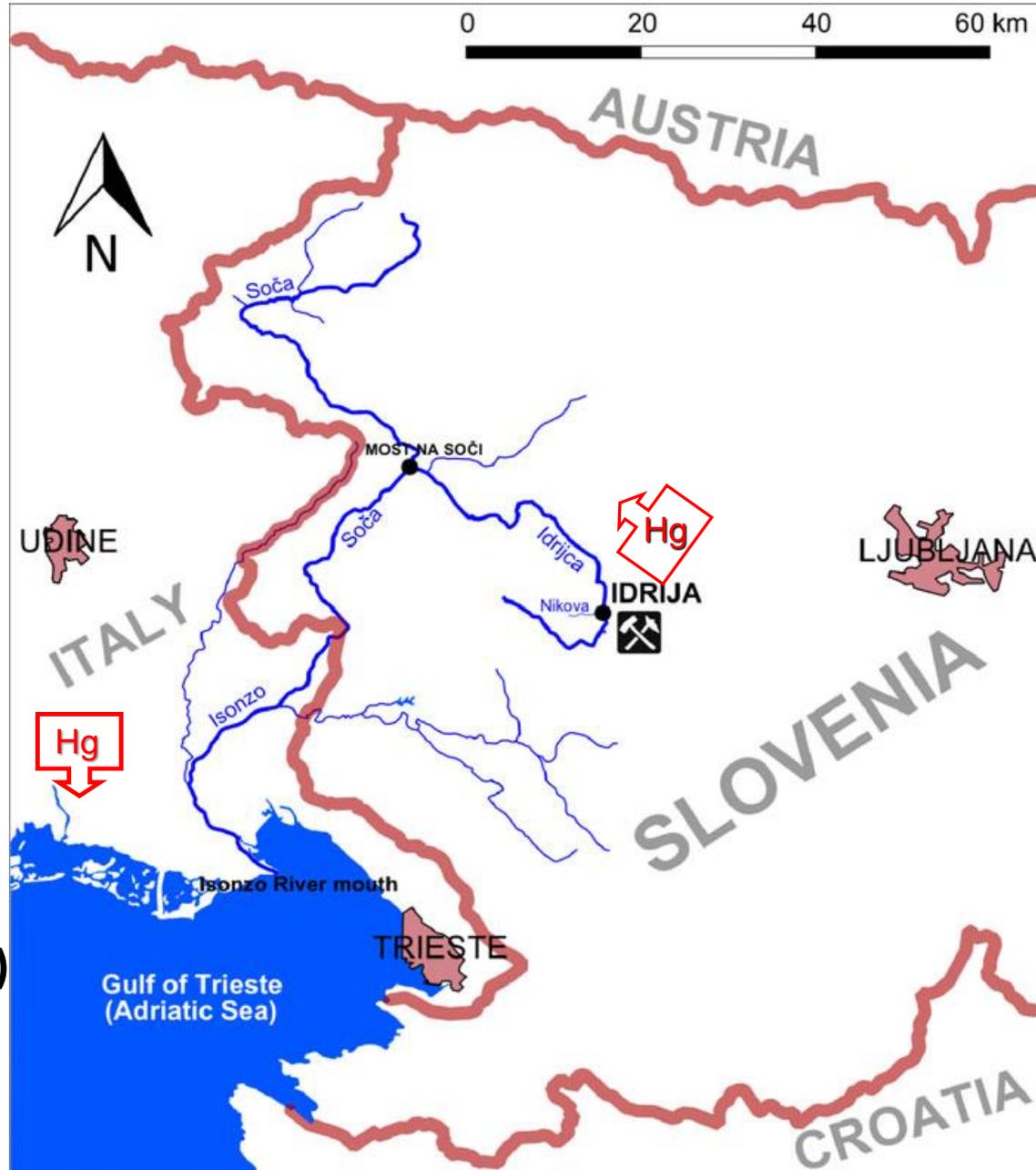
Miniera di Idria



Fiume Isonzo  
(circa 500 anni)

2) recente:

Impianto cloro-soda (Torviscosa)  
Sversamenti incontrollati  
(1930-84)

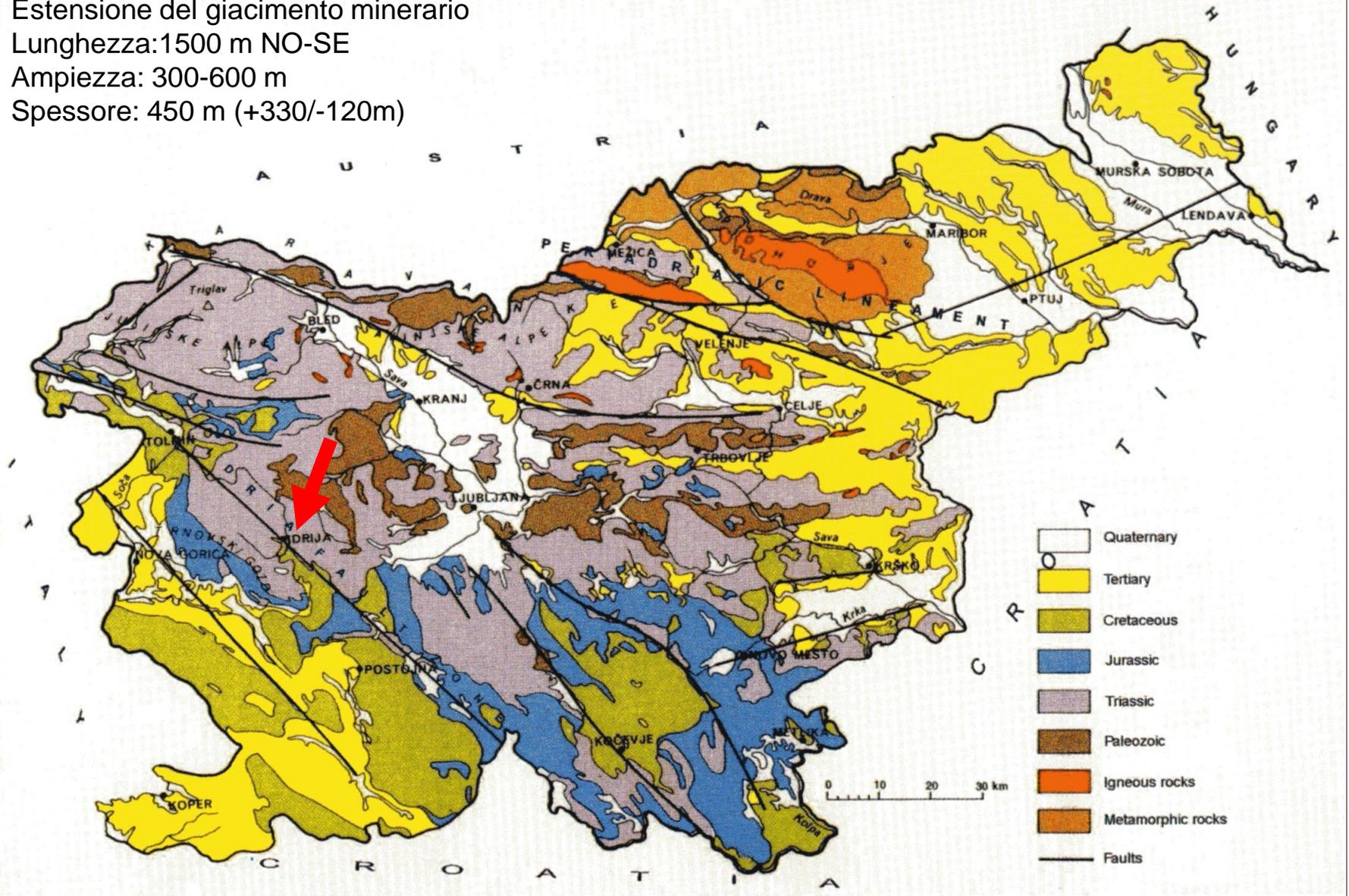


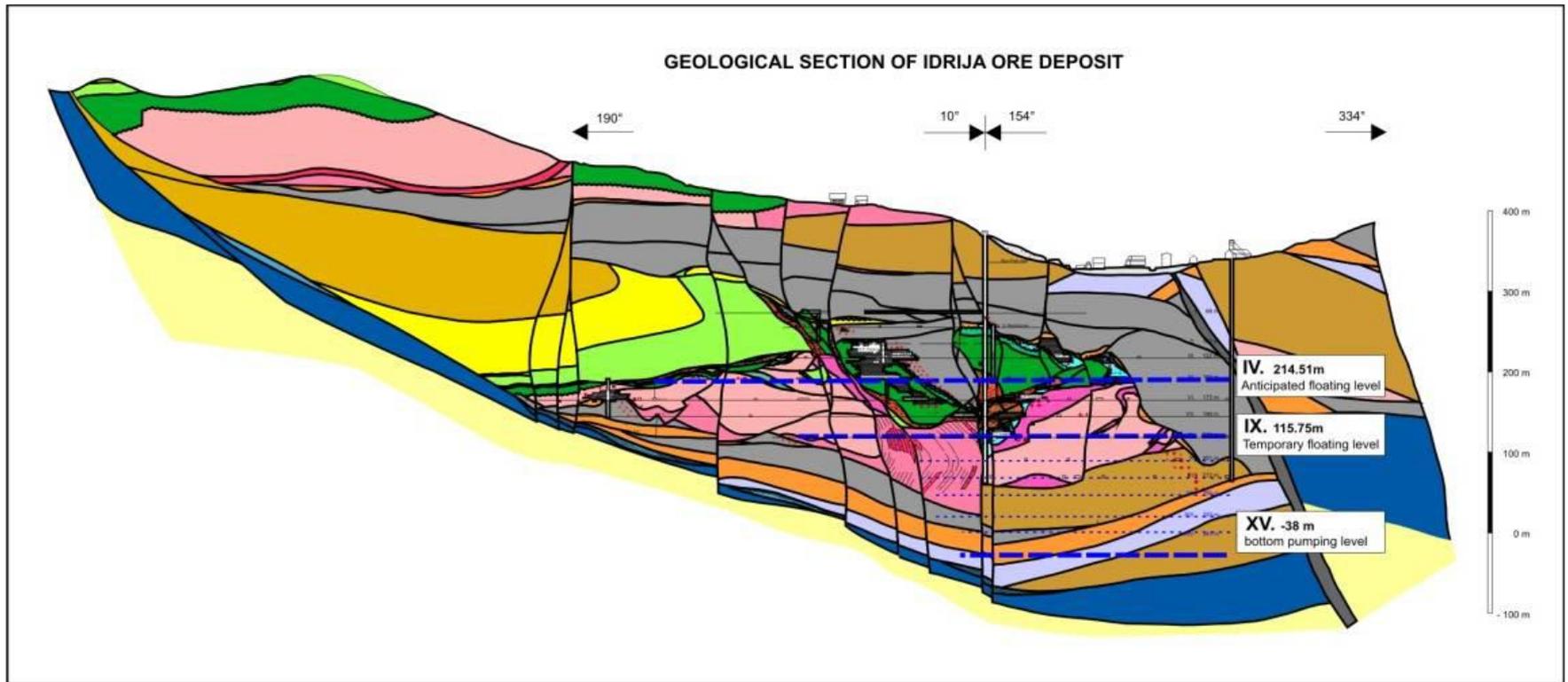
Estensione del giacimento minerario

Lunghezza: 1500 m NO-SE

Ampiezza: 300-600 m

Spessore: 450 m (+330/-120m)





Tipologia delle mineralizzazioni: deposizioni da soluzioni idrotermali (depositi singenetici ed epigenetici) attraverso il sistema di faglie NO-SE

158 corpi mineralizzati (141 a cinabro) in scisti carboniferi, calcari e dolomie (Permiano-Triassico inf.-medio)

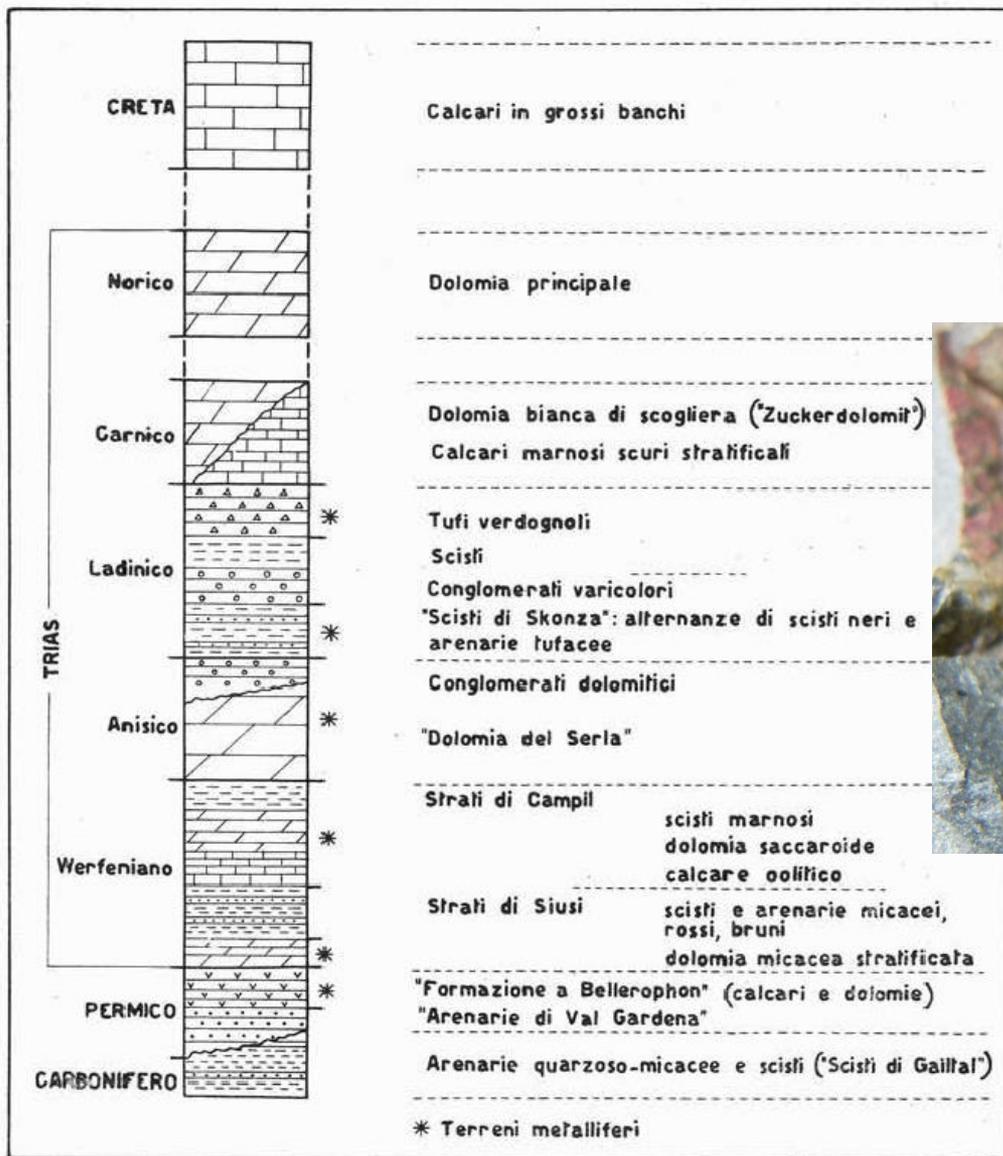
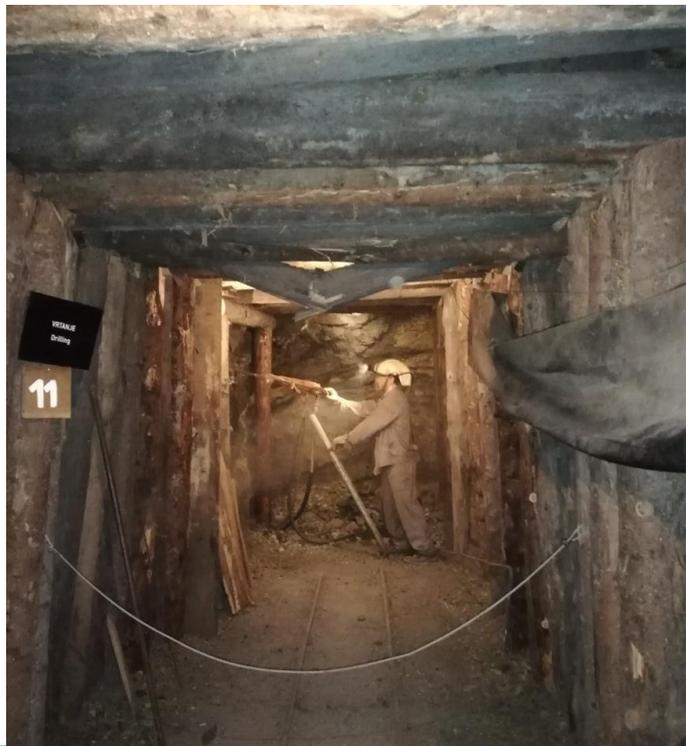
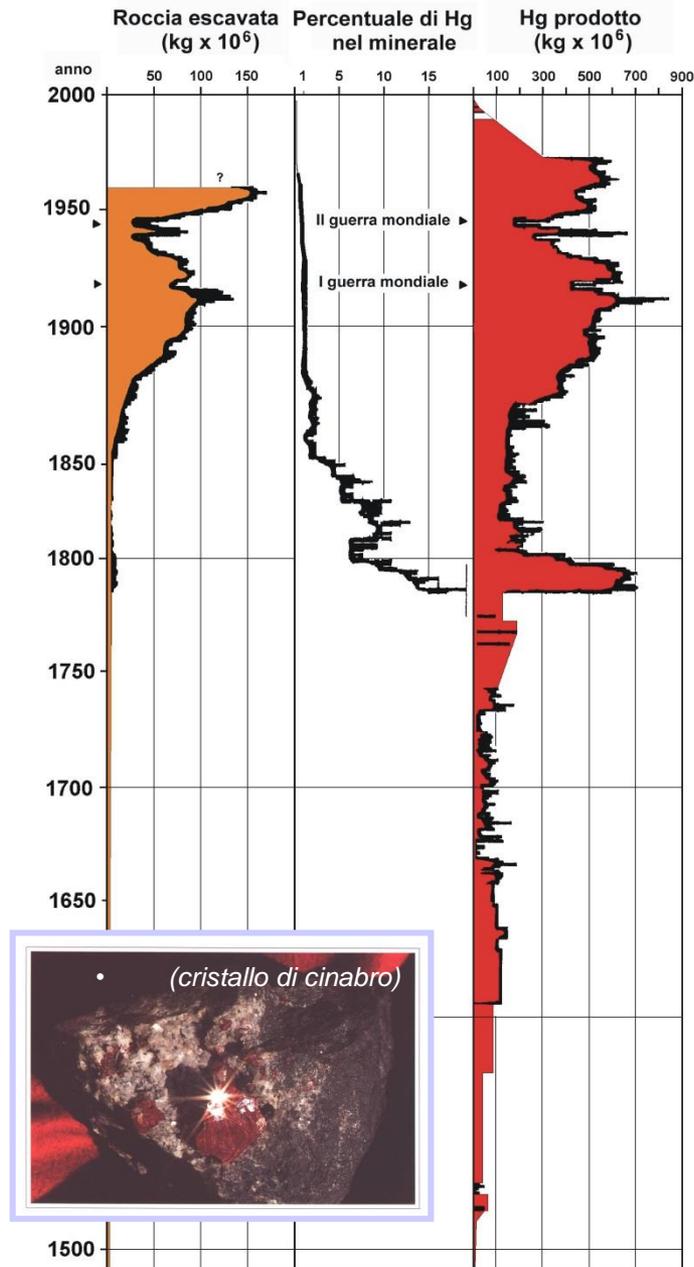


Fig. 2. — Colonna stratigrafica, in scala approssimata, dei terreni che compaiono nella zona cinabrifera.



# L'attività mineraria a Idria



• (da Mlakar, 1974)

- Oltre 5 milioni di tonnellate: è il quantitativo di roccia mineralizzata estratta, principalmente sotto forma di cinabro, in 500 anni di attività nel distretto minerario di Idria (Slovenia).
- 105.000 tonnellate: è la quantità di Hg metallico prodotto durante i processi di arrostitimento del minerale.
- 73%: è la percentuale stimata di Hg estratto. La restante parte è stata rilasciata nell'ambiente circostante.

The roasting process produced gaseous and particulate matter emissions, which were the major cause of the huge geochemical halo around the Idrija mercury mine (Gosar and Sajn, 2003; Gosar et al., 2006).



max emissione dal camino  
dell'impianto: 20 kg Hg/giorno  
(Kosta et al., 1974)









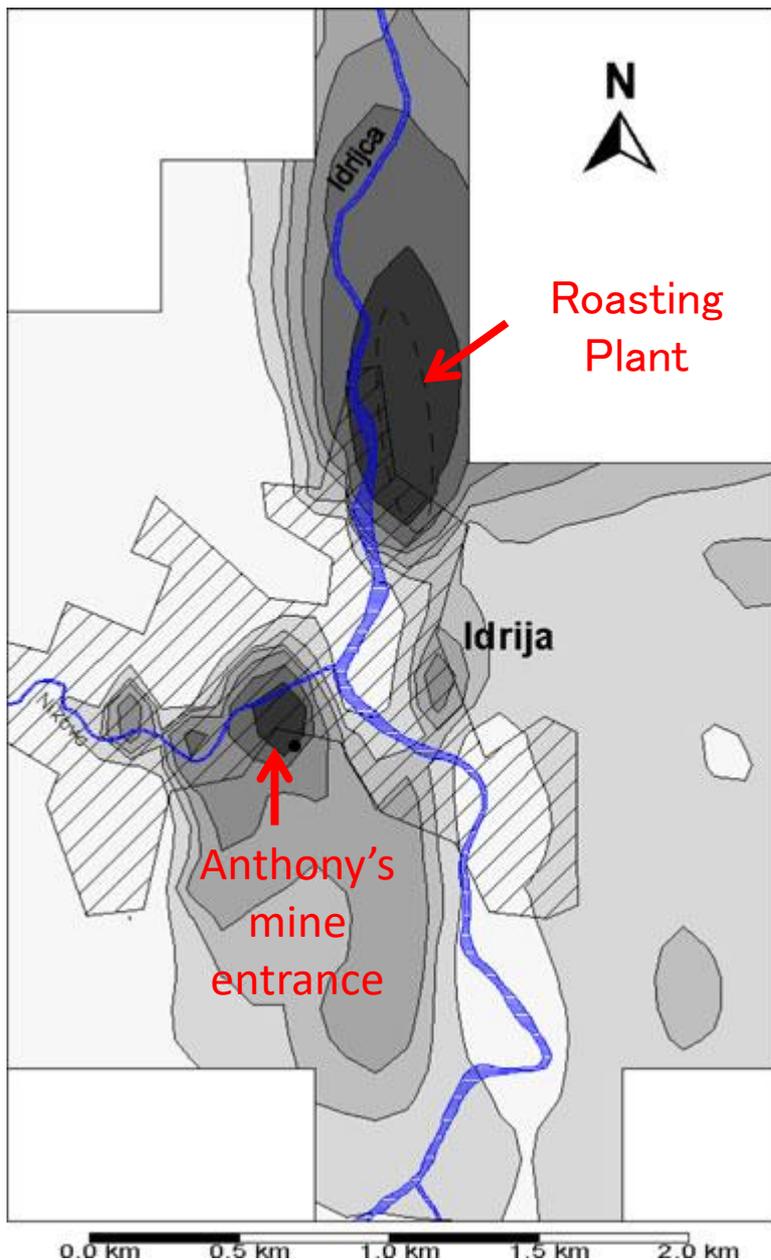
ELEKTRICNA PREVODNOST

GOSTOTA 3

AGREGATNA STANJA Hg  
Aggregate states of mercury

Daso atóma je na  $293\text{ K}$ , pri  $20\text{ }^\circ\text{C}$  in ob  
normalnem atmosferskem tlaku, vedno tekoča snov.  
Mercurij je, ob  $20\text{ }^\circ\text{C}$  in pri običajni  
atmosferski tlaku, edina snov, ki obstaja v vseh  
trih agregatnih stanjih.





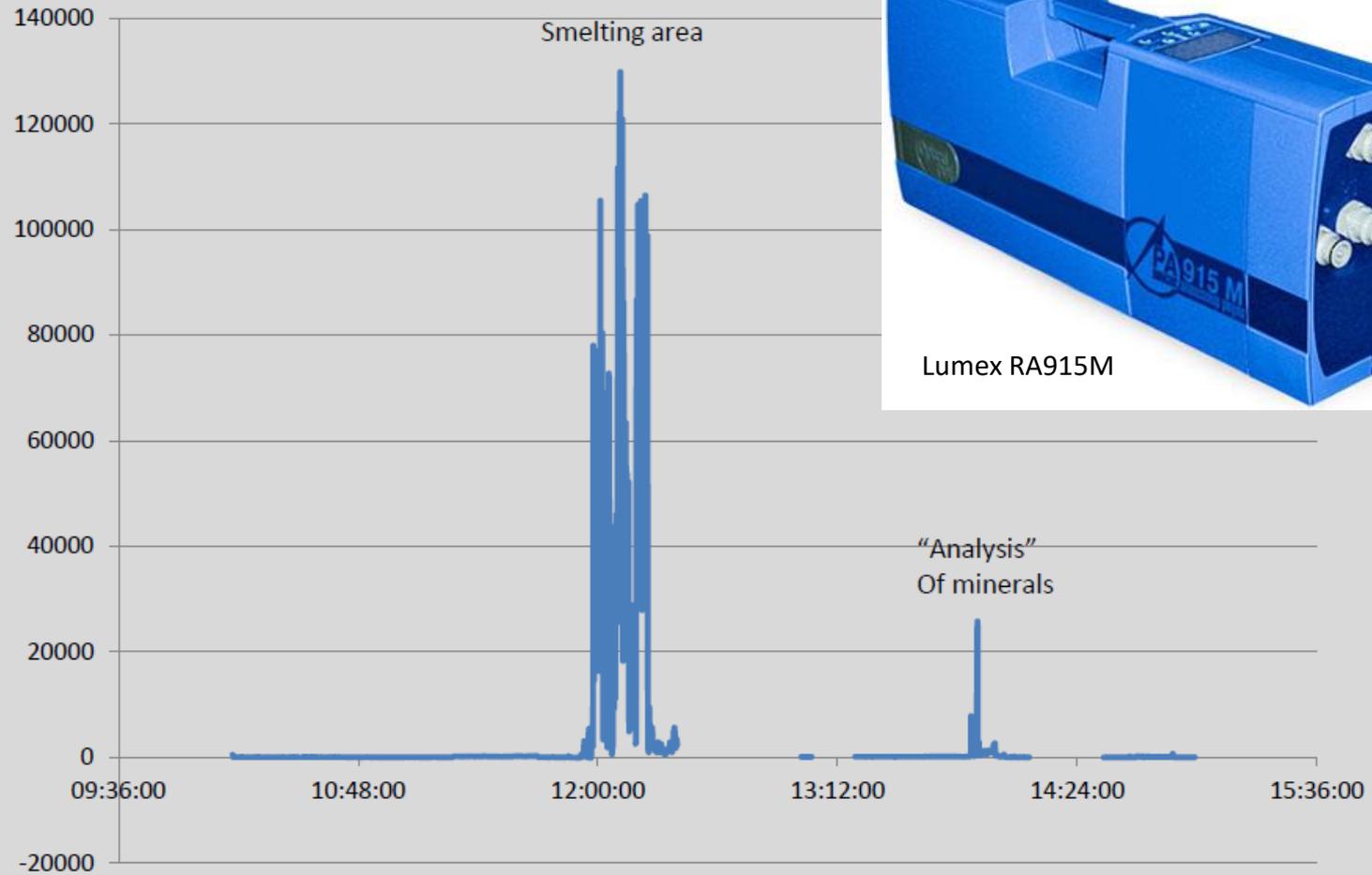
Geochemical map of **Hg distribution in the air** over the Idrija district on September 24, 1994 (Gosar et al. 1997a, b): the ore processing was stopped 10 months before.

Concentrations above 300 ng Hg/m<sup>3</sup> (in places even up to 2,000 ng Hg/m<sup>3</sup>) were observed in the surroundings of the two main sources of mercury vapors in Idrija. The highest value (4,078 ng Hg/m<sup>3</sup>) was measured near the roasting plant.

During the 1970s, at the time of full production of the mine and roasting plant, concentrations of 10,000–30,000 ng/m<sup>3</sup> were found at the roasting plant courtyard.

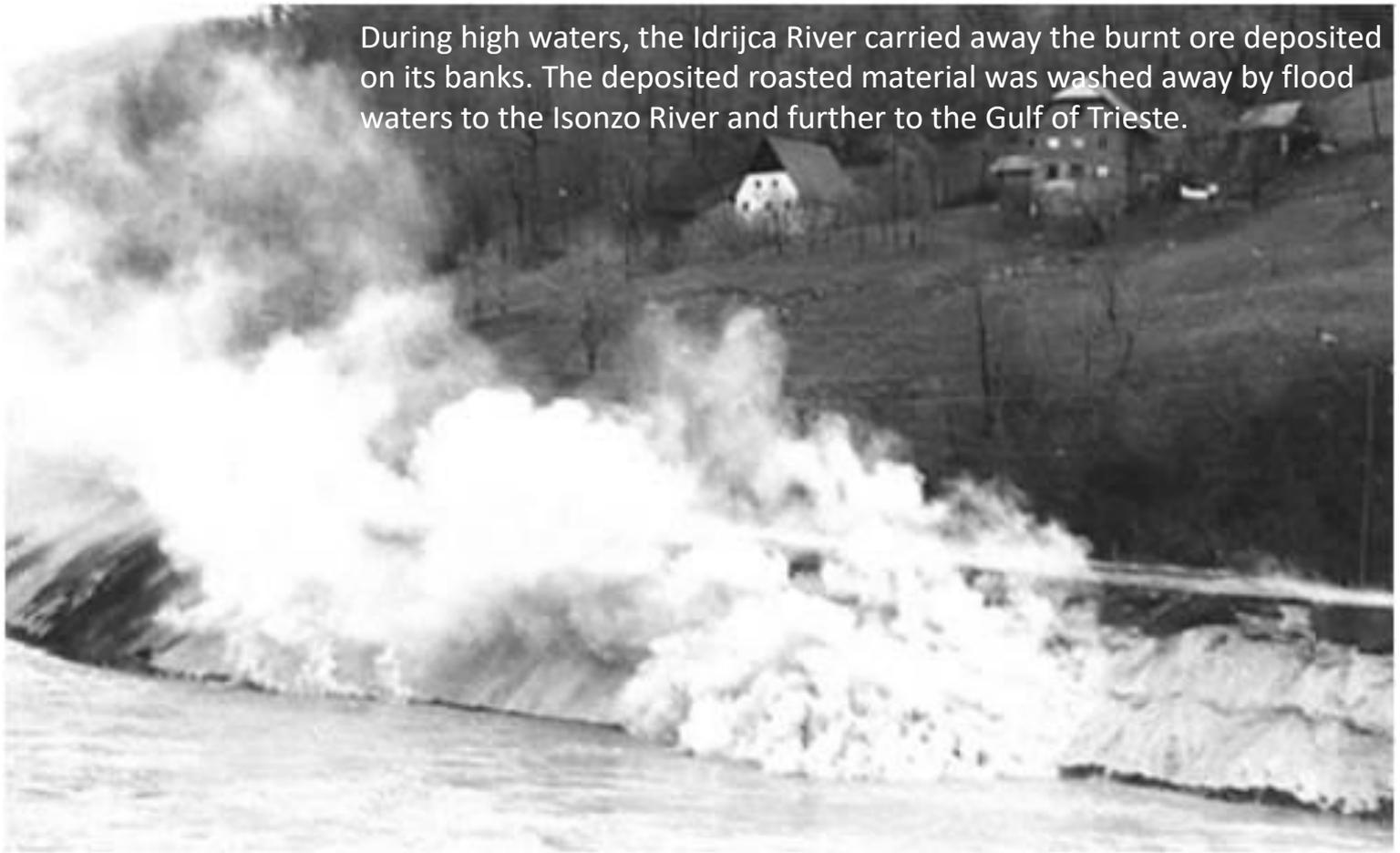
Recent times: significant Hg levels were found along the Idrija valley (25–50 ng/m<sup>3</sup>) and near Anthony's mine entrance (up to 200 ng/m<sup>3</sup>) in the vicinity of a carboniferous shale natural outcrop. Near the former roasting plant, Hg concentrations increased rapidly and reached 2,000 ng/m<sup>3</sup> (Kotnik et al. 2005).

# Hg concentrations in the visit to Idrija mine (06/05/2015)



Lumex RA915M

During high waters, the Idrijca River carried away the burnt ore deposited on its banks. The deposited roasted material was washed away by flood waters to the Isonzo River and further to the Gulf of Trieste.



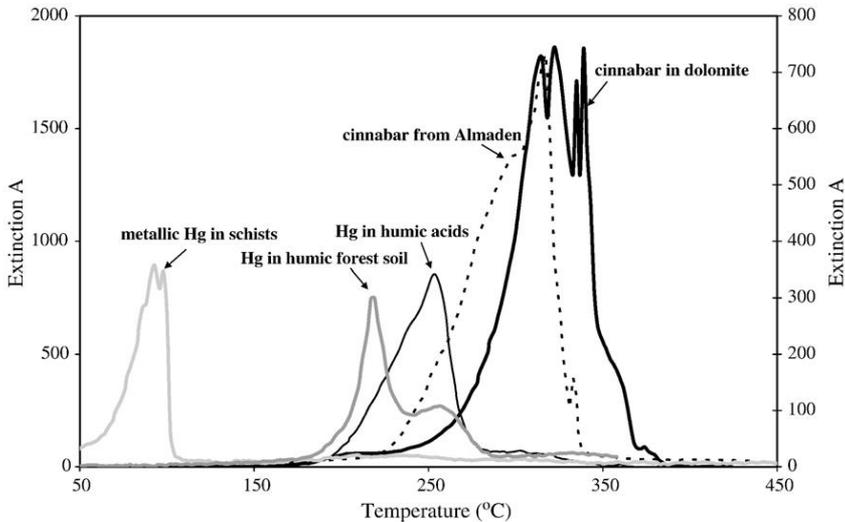
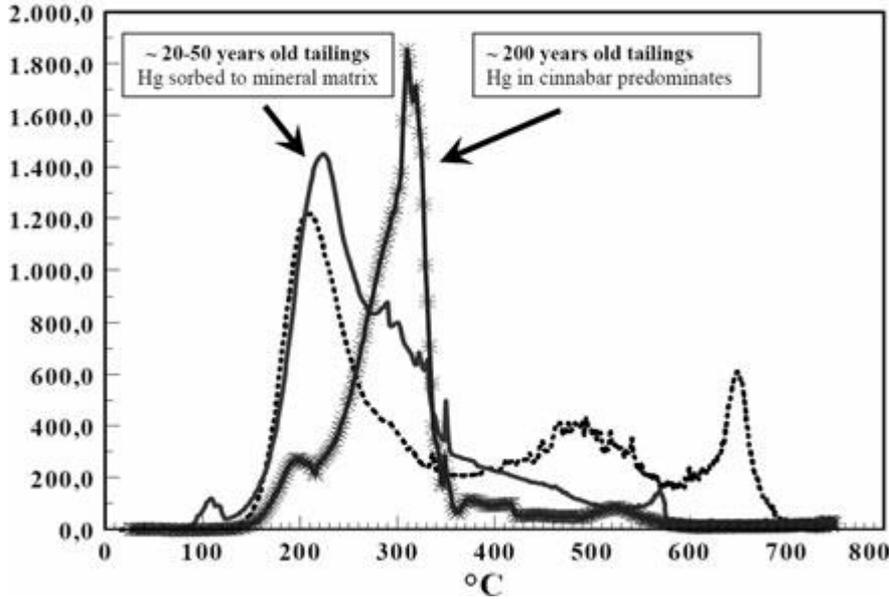
Inizialmente il **tasso di recupero dei metodi di estrazione di Hg** era il 50 %, poi 70-75 % dal 1867 al 1948

Con l'introduzione delle moderne fornaci rotative, il recupero è salito al 90%. Nuove discariche di residui di minerale calcinato sulla riva destra del fiume Idrijca (Čar 1998).

L'aumento della produzione di Hg portarono a problemi nello smaltimento

# Mercury remaining in tailings

Extinction A



Hg-thermo-desorption curves of standard materials

Using Hg thermo-desorption technique, Biester et al. (1999) found out that in older roasted ore residue dumps, the predominant Hg species was cinnabar (HgS) due to incomplete roasting, whereas in residue dumps of the twentieth century, the amount of cinnabar in the material was lower due to higher efficiency of the roasting process and the increasing use of ores bearing native Hg.

Mercury remaining in these younger residues mostly exists as metallic Hg, either adsorbed to matrix components or organically bound Hg formed by humic acids percolating through the residues from overlaying soils.

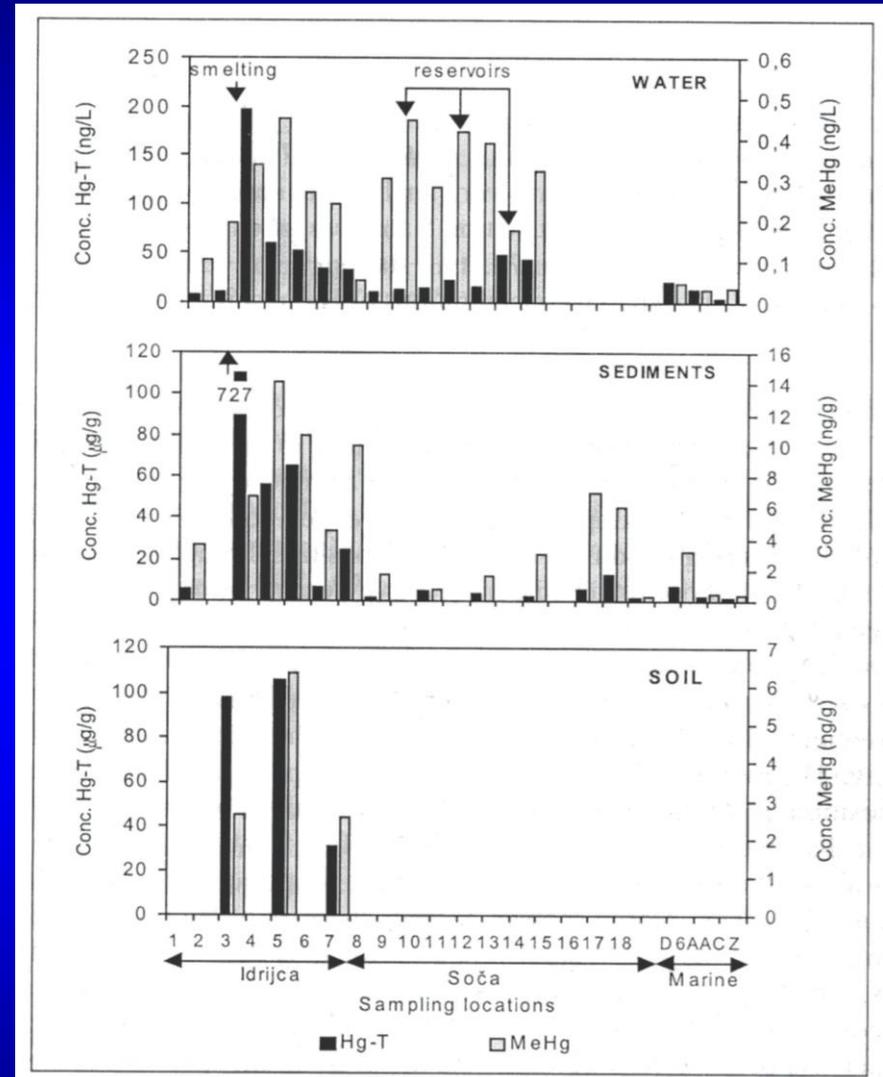
Leaching tests showed that in younger residue dumps, high amounts of soluble Hg existed in reactive form (more mobile and bioavailable).

# Hg nelle acque, nei sedimenti e nei suoli del sistema fluviale Isonzo-Idrija



Continuo input di Hg dall'area mineraria, dai suoli e dagli scarti di lavorazione del minerale (*tailings*) erosi dalle sponde del torrente.

Processi di trasformazione del Hg (es. metilazione) hanno luogo nei bacini artificiali lungo l'Isonzo



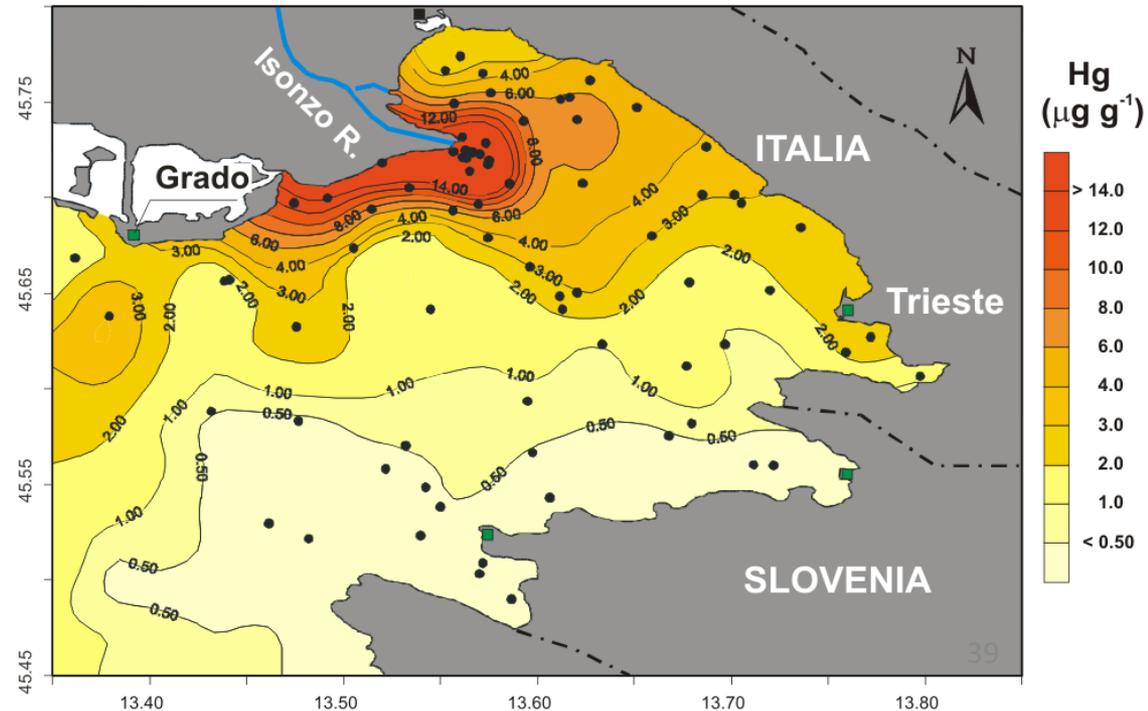
Horvat et al. (2002)

# Golfo di Trieste

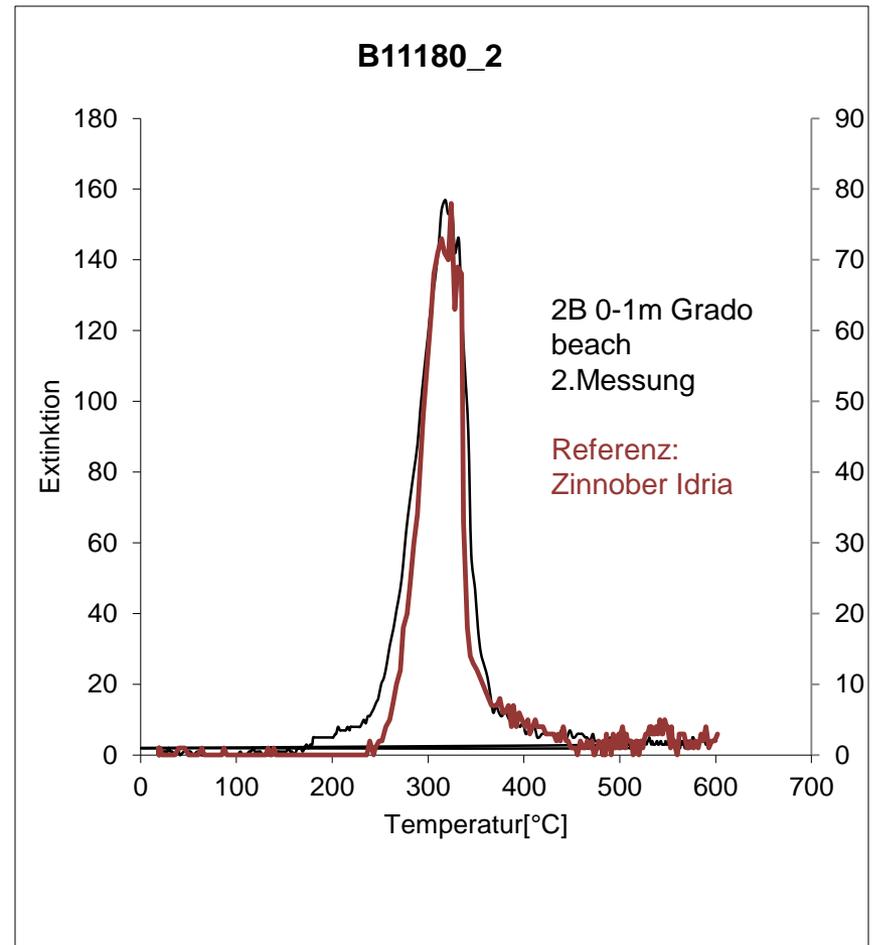
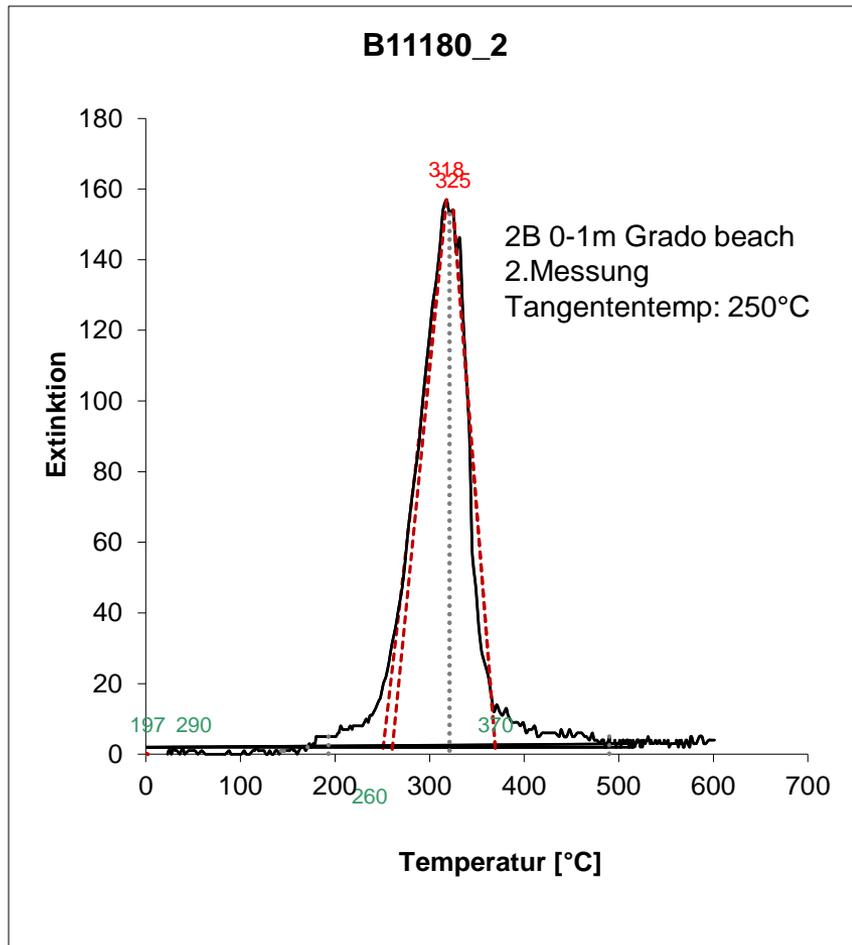
*Le piene fluviali del  
Fiume Isonzo apportano  
sedimenti e...*



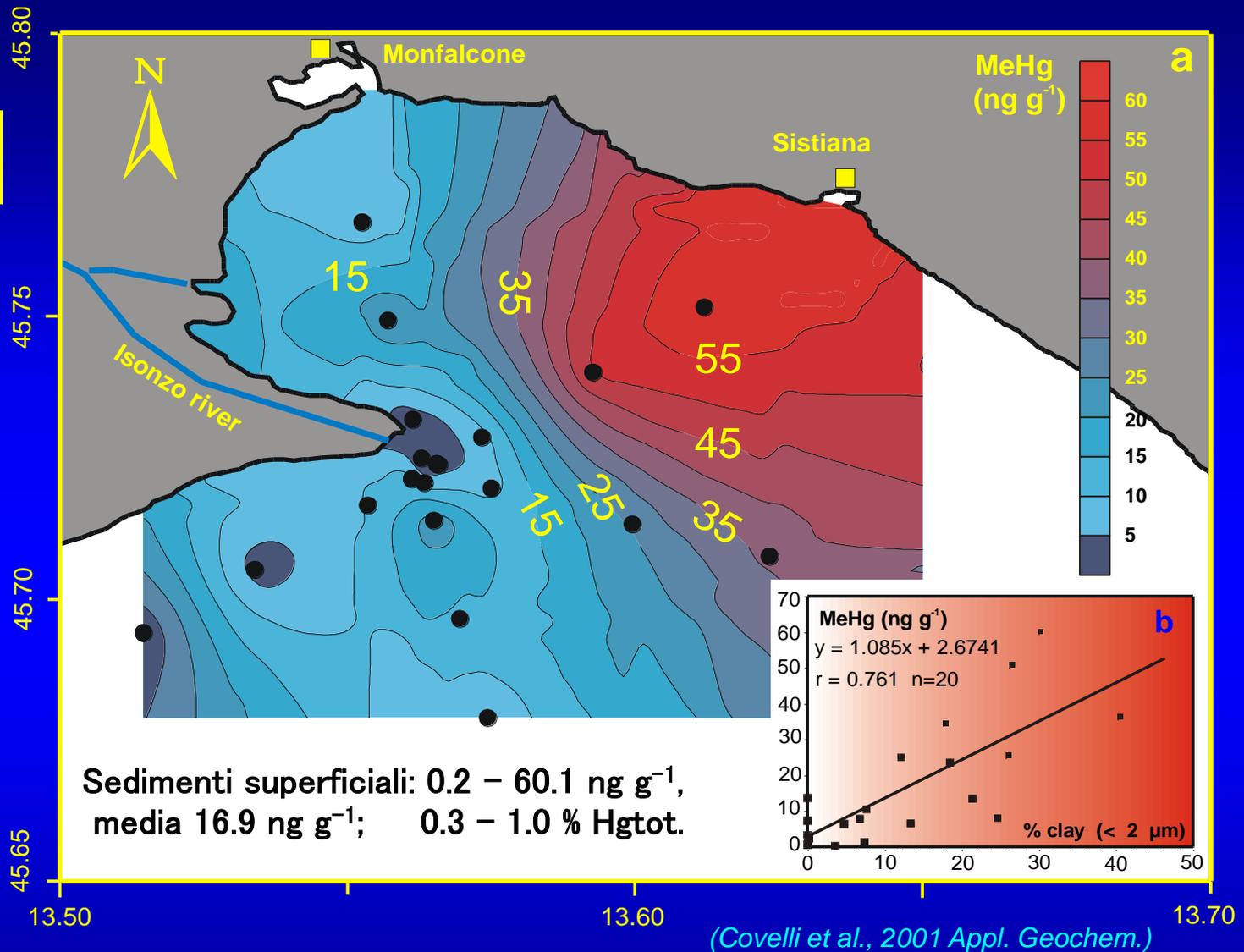
*....Mercurio  
che si accumula nei  
sedimenti superficiali  
del Golfo di Trieste ma  
non solo...*



## 2B 0-1m Grado beach



# Metil-Hg



- Concentrazioni più elevate di Metil-Hg nei fondali più distanti dalla foce fluviale isontina, caratterizzati da sedimento fine e maggior contenuto di sostanza organica.